TECHNICAL REPORT 1935 April 2006

Modeling Copper and Biocide Concentrations from Hull Paint Leachate in San Diego Bay

P. F. Wang D. B. Chadwick C. Johnson J. Grovhoug

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SSC San Diego

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ADMINISTRATIVE INFORMATION

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EXECUTIVE SUMMARY

As part of the U.S. Navy's antifouling (AF) program, a scientific team from SPAWAR Systems Center San Diego (SSC San Diego) conducted studies to evaluate low copper release coatings and non-metal, non-persistent biocide AF coatings, including Seanine, AF025, and AF028. The team used computer models previously developed and calibrated to simulate existing copper concentrations in San Diego Bay, as well as predicted concentrations of copper, Seanine, AF025, and AF028 resulting from designed implementation of non-metal and non-persistent biocides. Model results provided reliable and scientific data that quantified cause-and-effect relationships between bay water contaminant concentrations and sources from ship hull paint leachate. Modeling approaches in this study were used to justify risk-management decision-making scientifically.

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BACKGROUND

Accumulated marine fouling on the underwater hull surfaces of U.S. Navy vessels leads to adverse operational effects such as reduced speed, increased propulsive fuel consumption, increased hull cleaning and refueling, and reduced operating range between refueling. The U.S. Navy's antifouling (AF) program has sought to find AF-effective coatings that increase the time between hull maintenance periods (current goal is 12 years) and that are being environmentally safe. The Uniform National Discharge Standards (UNDS) program is now developing goals to reduce various ship emissions, including copper released from U.S. Navy ship hulls. Copper release from AF coatings represents about 63% of the total release from all ship sources in San Diego Bay. In addition, current ablative copper AF coating release rates are high and performance is marginal. Naval Sea Systems Command (NAVSEA) 05M has proposed a threepath program that includes continuing development and testing of non-toxic fouling release coatings, evaluation of low copper release coatings, and evaluation of non-metal, non-persistent biocide AF coatings, including Seanine, AF025, and AF028. Reducing or eliminating copper is a major benefit of all three approaches. As part of this effort, a scientific team from the SPAWAR Systems Center San Diego (SSC San Diego) Marine Environmental Quality Branch (Code 2362) provided technical support to NAVSEA 05M to evaluate the predicted concentrations of existing copper coatings and new, commercially available non-metallic AF coatings. This effort provided an environmental loading, contaminant fate, and transport prediction analysis that will demonstrate a technical approach to characterize predictive modeling for copper and organic biocides for two U.S. Navy harbors, San Diego Bay (Fiscal Year [FY] 2000) and Pearl Harbor (FY 2001).

INTRODUCTION

Copper in estuaries, including major U.S. Navy harbors, has been an issue of concern for its toxicity to marine organisms. Field data show that copper concentrations in San Diego Bay have been close to or above water quality criteria, gradually increasing from the lowest concentrations (<1 ppb) in the mouth region to ~2.5 ppb in the innermost region. Several hot spots with elevated concentrations exceeding the water quality criteria of 3.1 ppb exist, in particular, the Shelter Island Marina and the West Harbor Island Marina.

Major sources for copper in San Diego Bay include leachate from copper AF paints from civilian craft and naval vessels, watershed runoff, power plant discharges, and other limited point sources. Estimates of the amount of copper entering into the bay from those sources totals ~25,000 kg/year. For this study, we applied two calibrated hydrodynamic and fate and transport models, SD-1D and TRIM2D (Tidal Residues Inter-tidal Mudflat Two-Dimensional) to simulate and predict copper concentrations in San Diego Bay for existing conditions and designed loading reduction scenarios.

The (one-dimensional steady-state model) SD-1D was developed by SSC San Diego under support of the Office of Naval Research and the Strategic Environmental Research and Development Program (Chadwick and Largier, 2000; Largier, Hollibaugh, and Smith, 1997). The SSC San Diego team used bay-wide salinity distributions to calibrate and verify the model, which provides a rapid way to evaluate average, steady-state distributions of conservative and non-conservative constituent distributions on a spatial scale of about 1 km. The model was run as a precursor to the more detailed model (TRIM) to establish reasonable estimates for copper loss rates to the sediment. We ran the model using an estimated range of copper loading to San Diego Bay and then estimated loss rates by adjusting the loss rate to provide a best-fit model solution compared to available copper concentration measurements for the bay (Katz, 1998).

During the past 5 years, SSC San Diego, collaborating with the U.S. Geological Survey (USGS), developed a 2D hydrodynamic and transport model (TRIM) for San Diego Bay. Calibrated and verified using measured and historical tide and current data (Wang et al., 1998), TRIM simulated in-bay copper concentrations. Once discharged (from hull AF leachate and point and non-point discharges) into the bay, copper mass undergoes a series of physical, biological, and chemical processes, including mixing, dilution and transport by ambient flows, speciation, complexation, and partitioning among different phases of particulate and dissolved copper. The SSC San Diego scientific team adopted a "package approach" in which total copper concentrations in the water column were simulated by calibrating against field data. In this approach, sources of copper include leachate from copper paints of civilian boats and naval vessels; watershed runoff, power plant discharges, and other limited point sources; and f copper losses caused by adsorption to particles and settling to the bottom.

Concentrations of three AF organic biocides (Seanine, AF025, and AF028) were also simulated because of the leachate from hull paints with the proposed biocides. The team used a method similar to the copper loading method to calculate leachate loadings from naval vessels and civilian boats. We also used leachate from naval vessels and civilian boats to simulate and evaluate concentrations of the three biocides.

LOADING ANALYSIS

The SSC San Diego team calculated external copper loadings from different sources, including AF leachate from commercial vessels, private craft and Navy vessels, and point and non-point discharge. Johnson, Grovhoug, and Valkirs (1998) provided copper mass and locations of these loadings for San Diego Bay. Table 1 provides recently collected data. These loadings were used as model inputs to simulate existing copper concentrations (baseline) in the bay.

COPPER LOADING

The two load reduction scenarios included (1) eliminating copper loading from leachate of U.S. Navy vessels, and (2) eliminating copper loading from leachate of U.S. Navy and commercial/civilian vessels. For these scenarios, loading from runoff and the San Diego Gas and Electric Power Plant discharges remained unchanged. Therefore, the two loading reductions reflect scenarios for (1) non-copper paints applied to all U.S. Navy vessels, and (2) non-copper paints applied to all U.S. Navy vessels and commercial/civilian craft. The team conducted model simulations and simulated copper concentrations for these two scenarios and compared them with existing copper concentrations.

ORGANIC BIOCIDE LOADING

The SSC San Diego team estimated the loading of the three biocides (Seanine, AF025, and AF028) from hull paint leachate. The chemical manufacturing company provided the information for the estimated loadings. Because these biocides are new products in testing for AF use in marine water, uncertainties exist in the chemical processes, including leach rates and decay rates in marine water. For each biocide, uncertainty in leachate rate produces three loading estimates: low, median (estimate provided by Sigma Coating), and high values. The manufacturing company provided a half-life that represented the decay rates, which covered the possible range of uncertainties for their behavior in marine water. Tables 2 and 3 show the three loading scenarios that result when these loading conditions are coupled with the three uncertainties in decay rates.

Table 1. Existing copper loadings in San Diego Bay¹

Sources	Mass Loading (Kg/year)	Remarks
Submarine Base San Diego (SUBASE)	1,166	Navy
SSC San Diego	17	Navy
Antisubmarine Warfare (ASW) Base, San Diego	17	Navy
Naval Air Station North Island (NASNI)	1246	Navy
Navy Amphibious Base (NAB), Coronado	223	Navy
Naval Station (NAVSTA), San Diego	7564	Navy
Shelter Island	2788	Civilian
America's Cup Harbor	913	Civilian
Harbor Island-West	2027	Civilian
Harbor Island–East	732	Civilian
Laurel Street	174	Civilian
Embarcadero	340	Civilian
Coronado Roadstead	87	Civilian
San Diego Waterfront–10 th Ave	242	Civilian
Glorietta Bay	446	Civilian
Civilian Shipyard	1197	Civilian
Fiddler's Cove	522	Civilian
SD Waterfront-24 th Street	242	Civilian
Coronado Cays	1406	Civilian
National City Marina	161	Civilian
Chula Vista Marina	1030	Civilian
Commercial Basin	539	Civilian
San Diego Gas and Electric	324	Civilian
Bay-wide storm water	1452	Runoffs
Atmospheric deposition	7	
Total	24,859	

¹ Port of San Diego. 1997. "Convention Center Dewatering History and Alternatives." Report presented to San Diego Regional Water Quality Control Board, San Diego, CA.

Table 2. Estimated loading ranges from leachate and degradation rates from naval vessels.

Sources	Mass Loading (Kg/year)					
	Sean	nine and AF025			AF028	
	Low	Median	High	Low	Median	High
SUBASE	15.1	85.6	151.5	18.4	98.8	184.4
SSC SD	0.4	2.0	3.5	0.4	2.3	4.3
ASW Base	0.4	2.0	3.5	0.4	2.3	4.3
NASNI	13.4	75.6	133.8	16.3	87.3	162.9
NAB	4.5	25.3	44.7	5.4	29.2	54.4
NAVSTA	108.2	611.40	1081.7	131.7	705.5	1316.9
Total	141.9	801.9	1418.7	172.7	925.2	1727.1
Degradation	2.77	0.69	0.35	5.55	1.85	1.11
Rate (/day)	(0.2)*	$(0.10)^*$	$(0.05)^*$			
*: Rates in parenthesis are for AF025						

Table 3. Estimated loading ranges from leachate and degradation rates from naval vessels and civilian boats.

Sources Mass Loading (Kg/year)						
	Seanine and AF025			AF028		
	Low	Median	High	Low	Median	High
SUBASE	15.11	85.6	151.5	18.4	98.8	184.4
SSC SD	0.4	2.0	3.5	0.4	2.3	4.3
ASW Base	0.4	2.0	3.5	0.4	2.3	4.3
NASNI	13.4	75.6	133.8	16.3	87.3	162.9
NAB	4.5	25.3	44.7	5.4	29.2	54.4
NAVSTA	108.2	611.4	1081.7	131.7	705.5	1316.9
Shelter Island	41.7	235.7	417.1	50.8	272.0	507.7
America's Cup Harbor	133.7	77.2	136.6	16.6	89.1	166.3
Harbor Island- West	30.3	171.4	303.2	36.9	197.8	369.2
Harbor Island-East	11.0	61.9	109.5	13.3	71.4	133.3
Laurel Street	2.6	14.7	26.0	3.2	16.9	31.6
Embarcadero	1.5	8.3	14.7	1.8	9.6	17.9
Coronado Roadstead	1.3	7.3	13.0	1.6	8.5	15.8
SD Waterfront-10 th Ave	5.1	28.6	50.6	6.2	33.0	61.6
Glorietta Bay	6.7	37.8	66.8	8.1	43.6	81.3
Fiddler's Cove	7.8	44.1	78.1	9.5	50.9	95.0
SD Waterfront-24 th St.	5.1	28.6	50.6	6.2	33.0	61.6
Coronado Cays	21.0	118.9	210.3	25.6	137.2	256.0
National City Marina	2.4	13.6	24.1	2.9	15.7	29.3
Chula Vista Marina	15.4	87.1	154.1	18.8	100.5	187.6
Total	307.3	1737.0	3073.1	374.1	2004.2	3741.2
Degradation Rate (/day)	2.77 (0.23)*	0.69 (0.1)*	0.35 (0.05)*	5.55	1.85	1.11
			esis are fo	r AF025		

MODELING ANALYSIS—SD-1D

MODEL DESCRIPTION

The one-dimensional, steady-state box model, SD-1D, provided an initial assessment of the copper balance in San Diego Bay and estimates of copper loss rates to the sediment. The team formulated SD-1D to provide a one-dimensional, steady-state solution to the balance of conservative and non-conservative constituents. The model formulates rapidly and has run-times that relate to more sophisticated numerical models, but it cannot simulate time-varying concentrations and has relatively coarse spatial resolution.

San Diego Bay is classified as a Mediterranean-type or low-inflow estuary (Largier, Hearn, and Chadwick, 1996; Largier, Hollinbaugh, and Smith, 1997). Freshwater inflow to the bay occurs infrequently during the winter and is insignificant during most of the year. This classification, combined with a warm climate and consistent westerly wind patterns, leads to a net evaporation of water from the bay. This net evaporation in turn causes the bay to become hypersaline. Thus, for most of the year, the balance between the increase in salinity caused by evaporation and the decrease in salinity caused by tidal exchange with the ocean determines the salt balance. This balance tends to reach a quasi-steady-state by July and persists until the first significant winter rains in November or December (Largier, Hollinbaugh, and Smith, 1997). These characteristics along with its relatively one-dimensional morphology (long and narrow), make San Diego Bay ideally suited for models such as SD-1D.

The SD-1D model solves the steady-state, advection-diffusion equation for San Diego Bay by assuming a balance between evaporatively driven advection and tidally driven mixing (diffusion). The team segmented the model into a series of boxes along the axis of the bay (Figure 1) and estimated the advective term based on long-term evaporation rates for San Diego Bay reported by Largier, Hollinbaugh, and Smith (1997). We estimated the tidal mixing coefficients based on best-fit to measured salinity distributions during periods of low freshwater input (Katz, 1998; Figure 2). The volume and cross-sectional boundaries of each box are based on the detailed bathymetric data for San Diego Bay. Once the segment characteristics were determined, we ran the model by imposing constituent loading conditions at each segment, imposing the boundary concentration at the ocean and specifying any non-conservative characteristics of the constituent. The model then solves the advection-diffusion balance by iteratively marching from the ocean boundary to the head of the bay and adjusting concentrations until achieving a steadystate mass balance. This steady-state solution based on measured salinity distributions has been successfully used in a broad range of estuarine settings (Fischer et al., 1979; Stommel and Farner, 1952; Dyer, 1974).

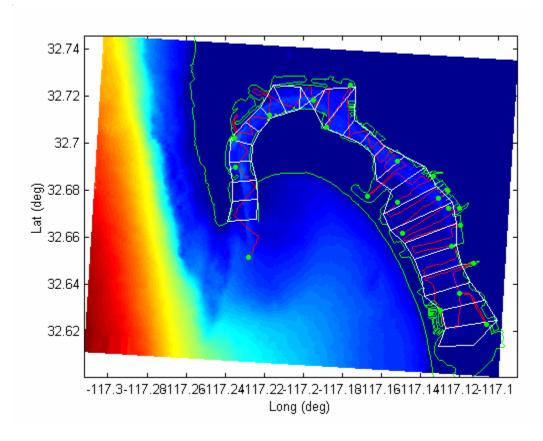


Figure 1. The segmentation for the SD-1D model superimposed over the bathymetry for San Diego Bay. The white boxes indicate SD-1D segments, the red line indicates the data measurement transect for the salinity calibration data set, and the green dots indicate the location of copper measurements.

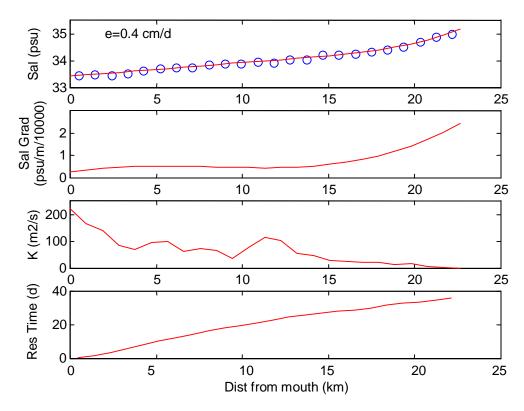


Figure 2. Model parameters for SD-1D, including (1) best-fit, segment-averaged salinity calibration data; (2) calculated salinity gradient; (3) tidal mixing coefficient; and (4) residence time, all as a function of distance from the mouth of the bay.

MODEL SETUP

The SSC San Diego team configured SD-1D with 25 segments for the Model Setup task. This configuration results in a spatial resolution of about 1 km, which is comparable to the spacing of available copper measurements in the bay (Figure 1). Copper loadings to each segment were determined based on the loading analysis described above. The boundary concentration at the ocean was estimated from measurement data as about 0.5 ppb (μ g/L). The team evaluated three loading scenarios, including (1) the existing baseline condition, (2) eliminating copper loading from all U.S. Navy hull coatings, and (3) eliminating copper loading from all U.S. Navy and civilian hull coatings. For each scenario, the team simulated a low, median, and high loading based on uncertainties in the measurement of hull coating copper leach rates. We used the baseline scenario in comparison to measured copper concentrations in the bay to estimate copper loss rates to the sediment. A range of loss rates was calculated based on the potential uncertainty in the loading data. These loss rates were then applied to the other scenarios and also used to formulate the TRIM2D model simulations.

MODELING ANALYSIS—TRIM2D

MODEL DESCRIPTION

The SSC San Diego team applied the numerical hydrodynamic and transport model, TRIM, to simulate the dilution and transport of effluents proposed for discharge into the bay. TRIM is a depth-averaged tidal and residual circulation model with a finite-difference numerical grid and scheme. TRIM has been previously applied to simulate time-varying water surface elevation and averaged water-column currents and associated transport of contaminants for several estuarine systems, including San Francisco Bay, CA; Boston Harbor, MA; Charleston Harbor, SC; and Venice Lagoon, Italy. Over the past 2 years, SSC San Diego has applied TRIM to several water-resource and water quality studies for San Diego (Wang et al., 1998).^{2, 3}

Using TRIM, a two-dimensional (2D), depth-averaged model, is justified because it is based on existing field data that show that flow in San Diego exhibits strong uniformity in the water column (Wang et al., 1998). Such uniformity of flow in the water column results primarily because flow in San Diego Bay is primarily driven by tides from the Pacific Ocean and San Diego Bay is shallow, which is a basic assumption associated with TRIM. Other assumptions in model formulation included the Boussinesq approximation and incompressibility. As with any depth-averaged model, velocity and density are implicitly assumed as nearly constant over the water column. However, horizontal density gradients are treated explicitly in the momentum equations. We approximated bottom shear stress using a Manning–Chezy formulation with Manning's n coefficient assigned as a function of water depth and assumed that water depth is sufficiently shallow so that the Ekman layer can be neglected (Cheng, Casulli, and Gartner, 1993). Thus, the direction of bottom shear stress is assumed as exactly opposite to the depth-averaged velocity.

An additional transport equation solving each species simulates solute transport. Solutes are assumed as dilute (no more than 1000 parts per million), thus the solute transport equations are uncoupled from hydrodynamics. Furthermore, the transport equation is solved one time-step behind the continuity and momentum equations, effectively uncoupling the transport equation (Cheng, Casulli, and Gartner, 1993). This approach is valid because baroclinic forcing changes less rapidly than barotropic forcing. The advective term in the transport equation is processed using an upwind differencing scheme that ensures conservation of mass as solutes are transported by advection. Similar numerical schemes have been used in several previous studies (Wang et al., 1997; Wang and Martin, 1991). For details about formulation and previous applications of TRIM, see the listed references.

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² D. B. Chadwick et al., 1996. "Sediment Quality Characterization Naval Station San Diego." Draft Final Report. San Diego, CA.

³ P. F. Wang, D. Sutton, K. Richter, and B. Chadwick. 2000. "Fate of Sediments and Sorbed Chemicals Resuspended by Ship Docking at Naval Station San Diego: A Stochastic Modeling Study." Submitted in International Conference on Hydraulics Research (ICHR)-2000.

To calculate TRIM, the team used the 1983 tide data collected by the National Oceanic and Atmospheric Association (NOAA) at Ballast Point, Downtown San Diego, and South Bay. We used tides collected at Scripps Piers as the boundary conditions for the model, which, along with the Manning's n coefficients, were fine-tuned to best-fit the model-simulated tides with measured values. Once calibrated, we ran the model for independent simulations and compared results with measured tides and currents for model validation. Overall, the difference between model and measurements range was about less than 3% for tidal heights and less than 15% for tidal currents. The differences in tidal currents between model and measurements may be attributed to multiple sources, including the errors associated with measurement and the three dimensionality of the flows that are approximated and simulated by the 2D, vertically averaged model (TRIM).

From a rest condition, we ran TRIM for 2 days (48 hours) to ensure that a steady-state flow condition was reached before the constant-load effluent entered into the bay. This initial 2-day run was necessary to eliminate transient flows that did not exist under the steady-state, quasi-repetitive tidal conditions. We used a 6-minute time-step in the model and simulated tidal height and tidal currents. Effluent concentration at each model grid were stored every 2 hours. Simulation for 1 year (365 days) was executed, which amounts to 4356 temporal snapshot vector data sets. The team conducted statistical analyses to the model results; the Modeling Results sections of this report discuss the findings from this modeling study.

MODEL SETUP

Two rectangular numerical grid systems (50 m x 50 m and 100 m x 100 m) are used for TRIM. Both grid results show little differences for simulated tides and currents. Therefore, only the results from the 100-m x 100-m grids are discussed. The numerical grids cover the entire San Diego Bay and portions of the ocean outside the mouth, consisting of 30,845 grid cells with 21,563 water cells. Measured tides are prescribed along the west, south, and north boundaries of the model domain.⁴

Once discharged into San Diego Bay, copper mass from those external loadings dilute and mix with ambient water. Copper (metals in general) in the bay exists in dissolved and particulate forms. The existing data are total load and do not differentiate dissolved and particulate forms. Since copper undergoes a series of chemical processes, including speciation, complexation, and adsorption to suspended solids, modeling these processes involves an elevated need for field data. In this study, an 8%-per-day net loss rate was used to account for loss of copper in particulate form to sediment bed through settling. This 8%-per-day loss rate is consistent with the predictive model results from SD-1D and the magnitude of field data observed by scientists over the years. Although in the box-model, SD-1D, a 7.4%-per-day loss rate was used to account for sediment loss rate, the difference (0.6% per day) bears little significance, because the data used for calibrating SD-1D are point measurements (Figure 1) and, therefore, may not represent the corresponding field data with the same spatial resolution.

⁴P. F. Wang and B. Chadwick. 1998. "Dilution and Transport of Convention Center Effluent of Copper, Zinc and Silver in San Diego Bay." SPAWAR Systems Center San Diego draft report for the Port of San Diego.

MODELING RESULTS: COPPER

SD-1D SIMULATIONS

Figure 3 shows the simulated copper concentrations for scenario (1), the existing baseline scenario. The SSC San Diego team simulated three loading estimates (low, median, high) based on the potential range of copper leach rates form hulls. A loss rate to the sediment was imposed for the median-loading case to provide a best-fit to the measured copper data in the bay. The results for the median-loading case show that copper is low near the mouth of the bay, increases toward the back of the bay, and then decreases slightly at the very head of the bay. A portion of the inner bay is generally exceeding the current ambient water quality copper criteria of $3.1 \,\mu\text{g/L}$. The best-fit loss rate for the median-loading baseline scenario was found to be about 7.4% a day. Simulations with no loss to the sediment (not shown) resulted in bay concentrations approaching $15 \,\mu\text{g/L}$, clearly out of line with measured concentrations.

Figure 4 shows simulated copper concentrations for scenario (2), elimination of U.S. Navy hull copper leachate. Removing this copper source lead to a general bay-wide reduction of copper concentrations, with the largest reduction in the middle to inner bay areas. The reduction brings all model segment copper concentrations below the water quality criteria. The maximum concentration calculated for this scenario is about 3 μ g/L at segment 25 at the very head of the bay. Note, however, that isolated areas of the bay near remaining sources (such as yacht harbors) would very likely exceed criteria (see TRIM2D results below).

Figure 5 shows simulated copper concentrations for scenario (3), the elimination of U.S. Navy and civilian hull copper leachate. Removing these copper sources leads to a large and general bay-wide reduction of copper concentrations, with the largest reduction in the middle to inner bay areas. The reduction brings all model segment copper concentrations well below the water quality criteria. The maximum concentration calculated for this scenario is about $1.4 \,\mu\text{g/L}$ at segment 25 at the very head of the bay. Note, however, that isolated areas of the bay near remaining sources may have somewhat higher concentrations but are likely to remain below water quality criteria.

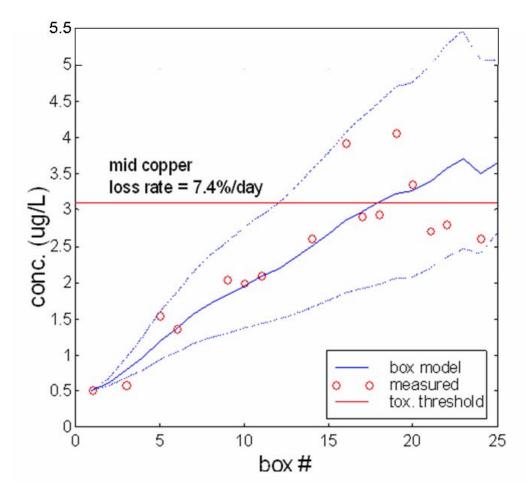


Figure 3. SD1D simulations of copper for scenario (1), the existing baseline loading condition in San Diego Bay. The three blue curves represent low, median, and high estimated copper leach rate conditions, respectively. Red circles indicate measured copper concentrations. The loss rate for the baseline median-loading case was determined by best-fit to the measured copper data.

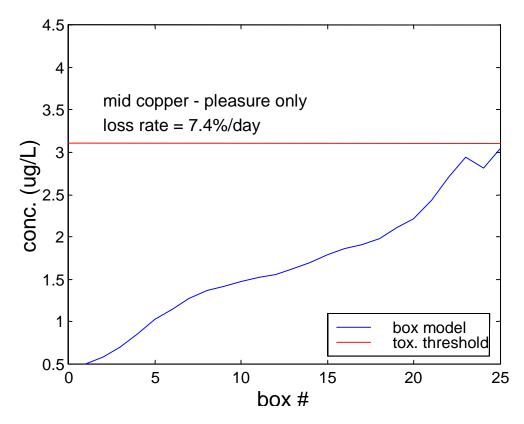


Figure 4. SD-1D simulation of copper for scenario (2), the removal of Navy hull leachate loading condition in San Diego Bay. The blue curve represents the median copper leach rate condition and the corresponding sediment loss rate. The red line is the current ambient water quality criteria for copper.

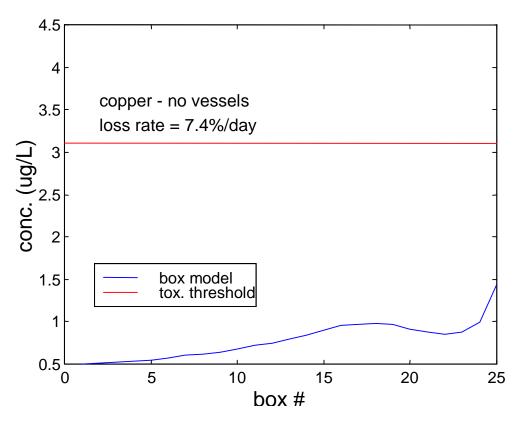


Figure 5. SD-1D simulation of copper for scenario (3), the removal of Navy and civilian hull leachate loading condition in San Diego Bay. The blue curve represents the median copper leach rate condition and the corresponding sediment loss rate. The red line is the current ambient water quality criteria for copper.

TRIM2D SIMULATIONS

Concentrations of copper were simulated over 1 year, while total copper mass inside the bay gradually reached a steady state. Figure 6 shows the steady-state copper concentrations in the bay under the existing loading conditions. Concentrations in most of the bay water are below the water quality criteria (3.1 ppb). However, simulated concentrations exceed the criteria in several locations (hot spots), including Shelter Island (~10 ppb), West Harbor Marina (8 to 9 ppb), Naval Station San Diego (~4.5ppb), and Coronado Cays (~8 ppb) (Figure 7).

With copper loads from the U.S. Navy vessels eliminated, simulated concentrations (particularly at the naval bases) are greatly reduced, with the largest reduction at Naval Station (~2.5 ppb) (Figures 8 and 9). However, the U.S. Navy load reduction, which constitutes ~45% of the total load to the bay, had almost no effect on concentrations in the marinas because these isolated waterbodies unfortunately have poor flushing characteristics and hold primarily private and commercial boats.

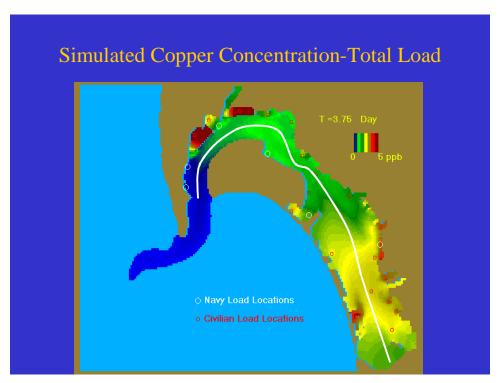


Figure 6. Simulated copper concentrations in San Diego Bay (existing condition).

Trim-Cu -Median Load-8%/d Loss Rate

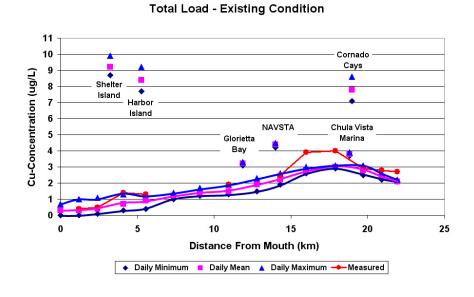


Figure 7. Simulated existing concentrations at locations with distance from the mouth and a few hot-spot waterbodies (along the white axial line in Figure 6).

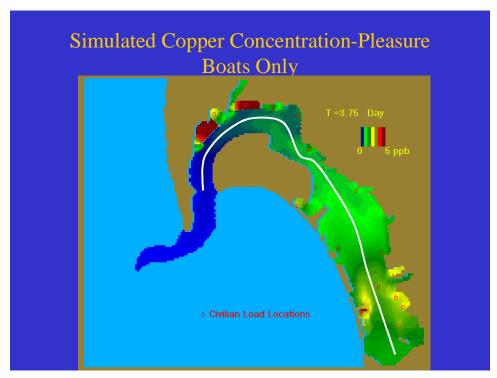


Figure 8. Simulated copper concentrations with no Navy vessel loads.

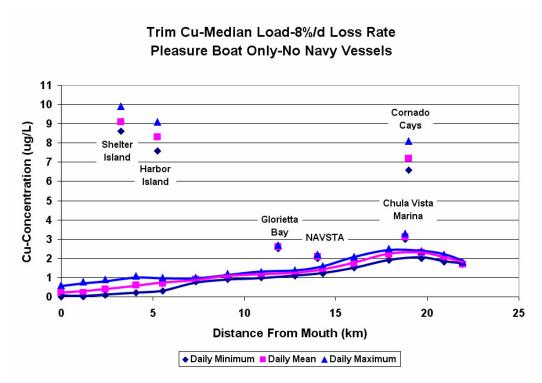


Figure 9. Simulated copper concentrations, with no Navy vessel loads, at locations with distance from the mouth and a few hot-spot waterbodies (along the white axial line in Figure 8).

For total reduction of copper loading from leachate from naval vessels and civilian boats, simulated copper concentrations are greatly reduced with concentrations at ~1 ppb (Figures 10 and 11). These residual concentrations result from loading from point and non-point sources, including runoff and power plant discharges are in the lower portion of the bay.

Figure 12 shows simulated copper concentrations for three loading scenarios: (1) existing conditions, (2) U.S. Navy elimination of copper AF coating load, and (3) elimination of U.S. Navy and civilian copper loading. Reducing copper concentrations near Naval Station San Diego would primarily result from reducing U.S. Navy copper loading, which would have little impact on elevated copper concentrations in heavily used yacht harbors such as Shelter Island Marina, West Harbor Marina, and Coronado Cays. Eliminating civilian boatloads would significantly reduce copper concentrations in those isolated marinas to levels well below water quality criteria.

Model results reveal that with all the loadings starting at low-ambient copper (<1-ppb) levels, steady states of copper in the bay are reached within 1 year with current loading projections. Conservatively, 1 year is the upper bound of flushing in the bay. Therefore, with the load reduction scenarios, the predicted copper concentrations also would reach their steady-state values before the year's end following the start of load reductions.

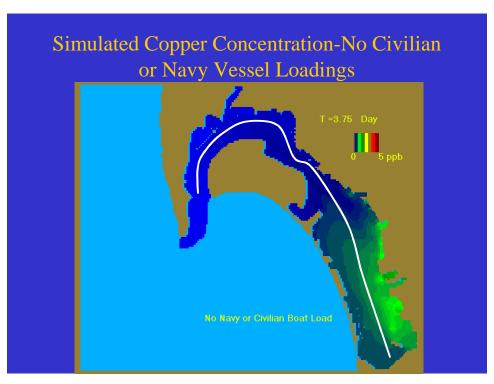


Figure 10. Simulated copper concentrations with runoff and power plant discharges only.

Trim-Cu-Median Load-8\$/d Loss Rate Cu-Load: Total, No Navy, No Navy/Civilian Load

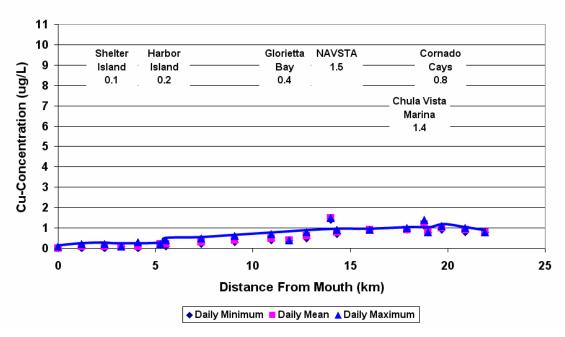


Figure 11. Simulated copper concentrations, with runoffs and power plant discharges only, at locations with distance from the mouth and a few hot-spot waterbodies (along the white axial line in Figure 10).

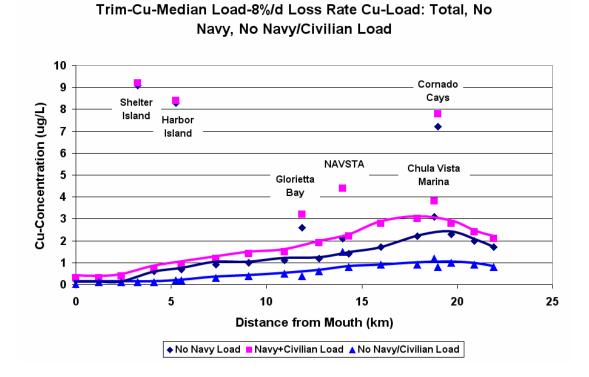


Figure 12. Comparisons of copper concentrations for three loading scenarios.

MODELING RESULTS: SEANINE, AF025, AND AF028

SD-1D SIMULATIONS

The SSC San Diego team simulated concentrations of Seanine, AF025, and AF028 for the three scenarios: low, median, and high. The low condition represents the lowest estimated leach rate and the highest estimated degradation rate for each coating. The median condition represents a mid-range leach rate and degradation rate, extrapolated from the data provided by Sigma Coating. The high condition represents the highest estimated leach rate and the lowest estimated degradation rate.

Maximum simulated Seanine concentrations caused by loading from naval vessels only ranged from <0.01 to about 0.09 ppb for the low and high scenarios, respectively. For the three scenarios, all locations in the bay were less than 0.1 ppb, well below the estimated toxicity threshold of 0.63 ppb (Figure 13). Maximum simulated AF025 concentrations caused by loading from naval vessels only ranged from <0.01 to about 0.3 ppb for the low and high scenarios, respectively. For the three scenarios, all locations in the bay were less than 0.3 ppb, well below the toxicity threshold of 1 ppb (Figure 14). Maximum simulated AF028 concentrations caused by loading from naval vessels only ranged from <0.01 to about 0.05 ppb for the low and high scenarios, respectively. For the three scenarios, all locations in the bay were less than 0.05 ppb, well below the toxicity threshold of 1 ppb (Figure 15).

Maximum simulated Seanine concentrations caused by loading from all vessels ranged from <0.01 to about 0.15 ppb for the low and high scenarios respectively. For the three scenarios, all locations in the bay were less than 0.16 ppb, well below the estimated toxicity threshold of 0.63 ppb (Figure 16). Maximum simulated AF025 concentrations caused by loading from all vessels ranged from <0.02 to about 0.6 ppb for the low and high scenarios, respectively. For the three scenarios, all locations in the bay were less than 0.7 ppb, below the toxicity threshold of 1 ppb (Figure 17). Maximum simulated AF028 concentrations caused by loading from all vessels ranged from <0.01 to about 0.07 ppb for the low and high scenarios, respectively. For the three scenarios, all locations in the bay were less than 0.08 ppb, well below the toxicity threshold of 1 ppb (Figure 18). The results from SD-1D represent average concentrations over large areas of the bay. Specific areas of high loading and/or poor flushing may have higher concentrations (see TRIM results).

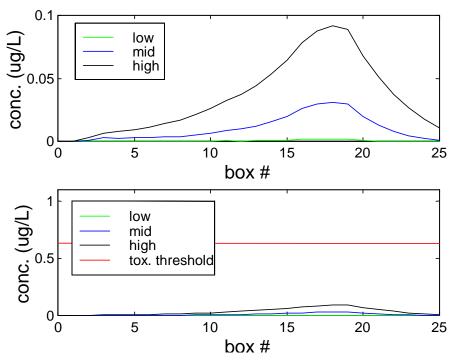


Figure 13. SD-1D simulated Seanine concentrations for low, median, and high (worst) scenarios (Table 2) for naval vessels only.

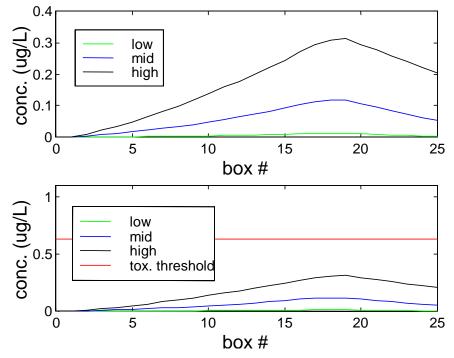


Figure 14. SD-1D simulated AF025 concentrations for low, median, and high (worst) scenarios (Table 2) for naval vessels only.

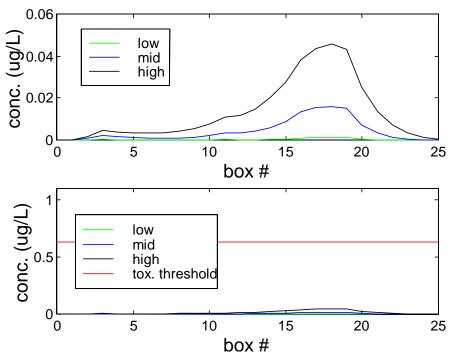


Figure 15. SD-1D simulated AF028 concentrations for low, median, and high (worst) scenarios (Table 2) for naval vessels only.

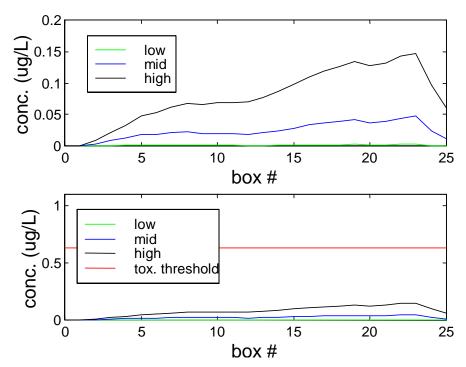


Figure 16. SD-1D simulated Seanine concentrations for low, median, and high (worst) scenarios (Table 2) for all vessels.

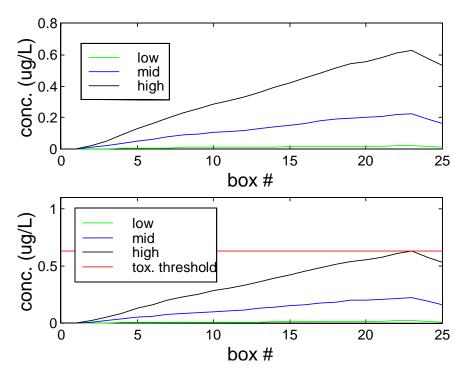


Figure 17. SD-1D simulated AF025 concentrations for low, median and high (worst) scenarios (Table 2) for all vessels.

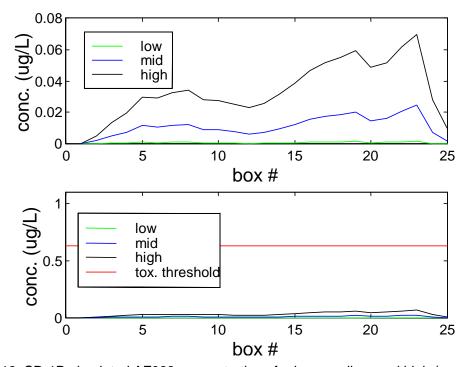


Figure 18. SD-1D simulated AF028 concentrations for low, median, and high (worst) scenarios (Table 2) for all vessels.

TRIM2D SIMULATIONS

The SSC San Diego team simulated concentrations of Seanine, AF025, and AF028 for two of the three loading scenarios (median and high loading). The low loading conditions result in simulated concentrations (<0.3 PPB) too low to be significant and, therefore, were not presented.

Simulated Seanine concentrations caused by biocide loading from naval vessels only were less than 0.1 ppb in the bay, well below the toxicity threshold of 0.63 ppb (Figure 19). Figures 20 and 21 show the simulated concentrations of AF025 and AF028, respectively, for median and high loading from naval vessels only. For both biocides, simulated concentrations were low throughout the bay, well below the toxicity threshold of 1 ppb.

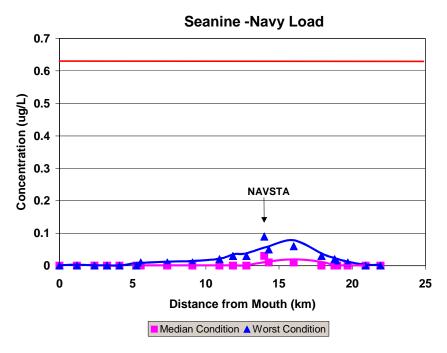


Figure 19. Simulated Seanine concentrations for median and high (worst) loading scenarios (Table 2) from naval vessels only.

AF025 -Navy Load Only

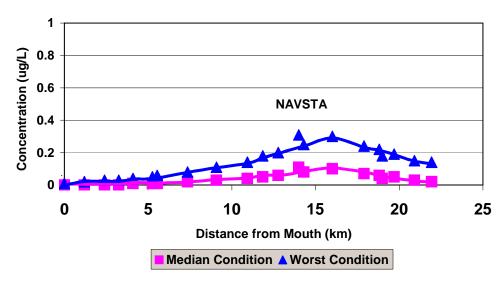


Figure 20. Simulated AF025 concentrations for median and high (worst) loading scenarios (Table 2) from naval vessels only.

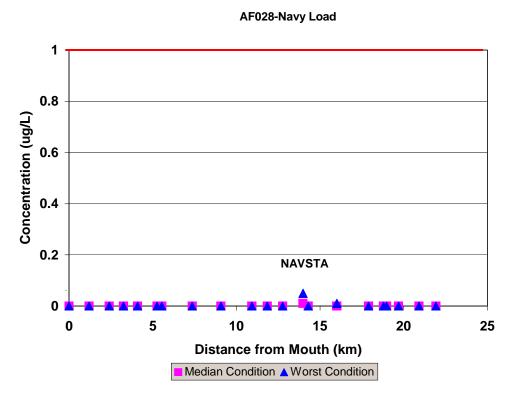


Figure 21. Simulated AF028 concentrations for median and high (worst) loading scenarios (Table 2) from naval vessels only.

For total loadings (naval vessels and civilian boats), simulated Seanine concentrations were in the range of 0.0 to 0.1 ppb, but with elevated values exceeding the 0.63-ppb toxicity threshold at several hot spots, including Shelter Island (0.6 to 1.3 ppb), West Harbor Marina (0.4 to 0.9 ppb), and Coronado Cays (0.7 to 1.3 ppb) (values in parentheses represent median and worst loading scenarios, respectively) (Figures 22 to 24).

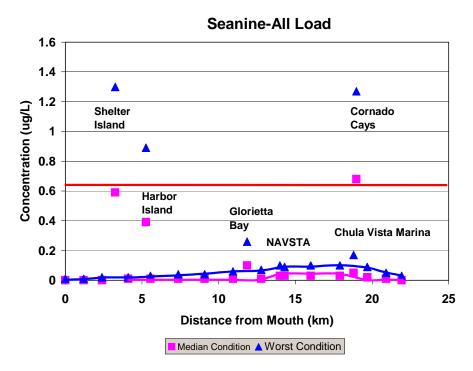


Figure 22. Simulated Seanine concentrations for median and high (worst) loading scenarios (Table 3) from naval vessels and civilian boats.

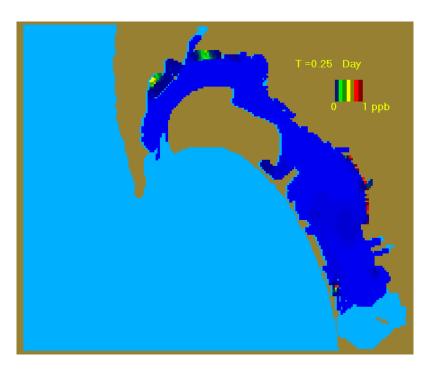


Figure 23. Simulated Seanine concentration contours for median loading scenario from naval vessels and civilian boats (Table 3).

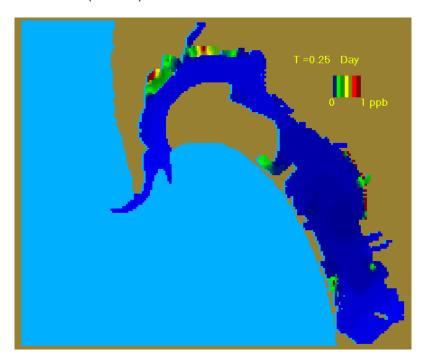


Figure 24. Simulated Seanine concentration contours for worst loading scenario from naval vessels and civilian boats (Table 3).

Figures 25 through 27 show the simulated AF025 concentration distributions and contours for the median and high loading scenarios from naval vessels and civilian boats. For Shelter Island, simulated AF025 concentrations exceeded the toxicity threshold (1 ppb) for median and high loading scenarios, while simulated concentrations in Harbor Island and Coronado Cays exceeded the toxicity threshold only under the high loading scenario.

AF025 -All Load 2.5 2 Concentration (ug/L) Shelter Island 1.5 Cornado Harbor Cays Island Glorietta Bay Chula Vista Marina 0.5 0 5 15 0 10 20 25 Distance from Mouth (km) Median Condition Worst Condition

Figure 25. Simulated AF025 concentrations for median and high (worst) loading scenarios (Table 2) from naval vessels and civilian boats.

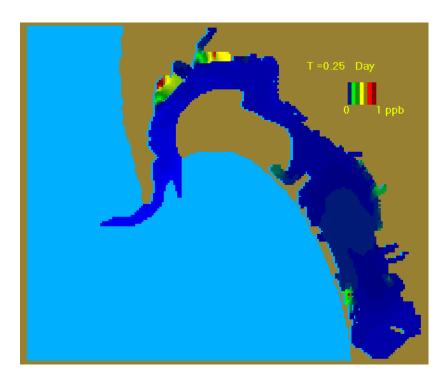


Figure 26. Simulated AF025 concentration contours for median loading scenario from naval vessels and civilian boats (Table 3).

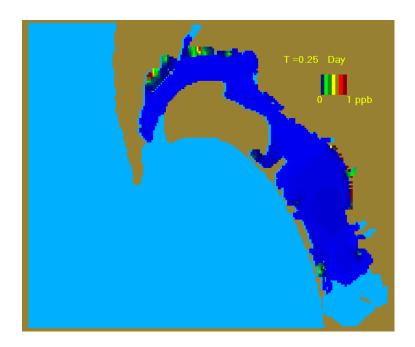


Figure 27. Simulated AF025 concentration contours for worst loading scenario from naval vessels and civilian boats (Table 3).

Figures 28 through 30 show simulated AF028 concentration distributions and contours for the median and high loading scenarios from naval vessels and civilian boats. Simulated AF028 concentrations were below the toxicity threshold (1 ppb) in most parts of the bay, except in Shelter Island and Coronado Cays, where predicted concentrations exceeded the toxicity threshold for the high loading scenario.

Table 4 summarizes the conditions of toxicity threshold exceedance for the three biocides under different loading scenarios. For Navy-only loading scenarios, we predicted concentrations of all three biocides to be less than the respective toxicity thresholds. For median loading scenarios from naval vessels and civilian boats, we predicted toxicity thresholds to be exceeded for Seanine in Coronado Cays, and for AF025 in Shelter Island. For high (worst) loading scenarios, we predicted toxicity thresholds to be exceeded for Seanine and AF025 in Shelter Island, Harbor Island, and Coronado Cays, and for AF028 in Shelter Island and Coronado Cays.

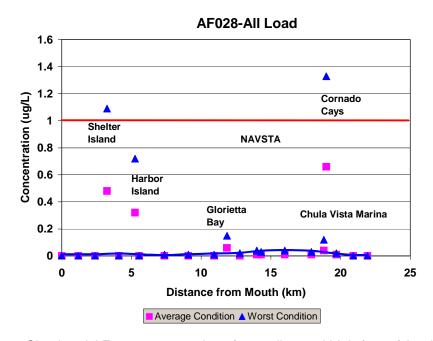


Figure 28. Simulated AF028 concentrations for median and high (worst) loading scenarios (Table 3) from naval vessels and civilian boats (Table 3).

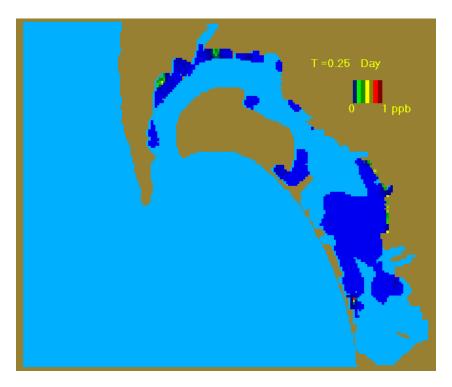


Figure 29. Simulated AF028 concentration contours for median loading scenario from naval vessels and civilian boats (Table 3).

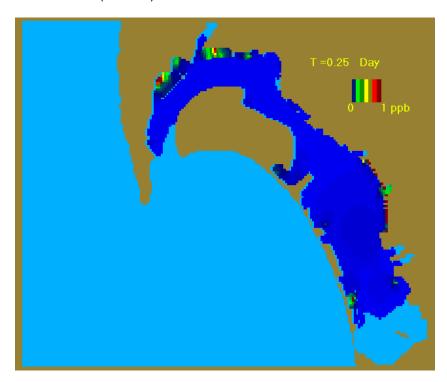


Figure 30. Simulated AF028 concentration contours for worst loading scenario from naval vessels and civilian boats (Table 3).

Table 4. Sub-waterbodies exceeding toxicity thresholds for different loading scenarios.

Everadores of	Nov. Only Londing	All	Loading	
Toxicity Thresholds	Exceedance of Navy-Only Loading (Median and High)		High (worst)	
Seanine (0.63 ppb)	None Coronado Cays		Shelter Island	
			Harbor Island	
			Coronado Cays	
AF025 (1 ppb)	None	Shelter Island Shelter		
			Harbor Island	
			Coronado Cays	
AF028 (1 ppb)	None	None	Shelter Island	
			Coronado Cays	

In summary, the SSC San Diego team successfully simulated concentrations of copper and three biocides (Seanine, AF025, and AF028) caused by hull paint leachate in San Diego Bay. The box model (SD-1D) and the more refined 2D hydrodynamic model (TRIM2D) produced consistent results for copper and the three biocides. While SD-1D established baseline results for major regions of the bay, TRIM2D provided detailed concentration contours, and "hot spots" with elevated simulated concentrations were identified. The models were further used to estimate concentrations in the bay water for designed load reduction/replacement scenarios. The modeling approaches adopted in this study can be applied to other similar studies in which risk management decision-making can be justified scientifically.

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14. ABSTRACT

As part of the U.S. Navy's antifouling (AF) program, a scientific team from SPAWAR Systems Center San Diego (SSC San Diego) conducted studies to evaluate low copper release coatings and non-metal, non-persistent biocide AF coatings, including Seanine, AF025, and AF028. The team used computer models previously developed and calibrated to simulate existing copper concentrations in San Diego Bay, as well as predicted concentrations of copper, Seanine, AF025, and AF028 resulting from designed implementation of non-metal and non-persistent biocides. Model results provided reliable and scientific data that quantified cause-and-effect relationships between bay water contaminant concentrations and sources from ship hull paint leachate. Modeling approaches in this study were used to justify risk-management decision-making scientifically.

15. SUBJECT TERMS

Mission Area: Environmental Science

copper concentrations non-metal and non-persistent biocides San Diego Bay risk management computer modeling antifouling coatings ship hull paint leachate

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